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Thermally stimulated conductivity in CaS : Pd phosphors

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CaS phosphors doped with Pd in varying concentrations have been prepared and their thermally stimulated conductivity (TSC) has been systematically studied in the temperature range of 300°K to 413°K. The effect of addition of activator on general features of the TSC curves is discussed and the activation energies have been estimated in two different ways. Conclusions are drawn regarding the type of kinetics involved in the recombination process.

1 Introduction

Despite considerable work that has been done on luminescence aspects of alkaline earth sulphide phosphors very little attention has been paid to their thermally stimulated conductivity behaviour. The measurements of TSC, which are relatively simple to perform, yield useful information about the trapping levels are recombination processes involved in the phosphor. Such studies have been made and reported recently on CaS phosphors activated with cerium (Vij & Mathur 1968) and co-activated with bismuth and dysprosium (Shalgaonkar *et al* 1972) However, the type of kinetics involved in the recombination process is not very clear The present study was made on CaS phosphors activated with varying concentration of Pd The object of the investigation was to measure the activation energy for samples containing varying concentration of Pd, and to study how this impurity influences the general features of the TSC curves Further, an attempt is made to determine the type of kinetics involved in the recombination process

2. Experimental

CaS : Pd phosphors of various concentrations were prepared by the method of thermal reduction of purified gypsum as followed by Bhawalkar & Malhotra (1969) The samples studied are listed in table 1.

The measurements of TSC have been made in the temperature range of 300°K to 413°K. A fixed quantity of phosphor was spread over a thick copper disc acting as a one electrode. The second electrode of copper was placed above the phosphor The sample was heated by a heating coil above which a mica sheet was placed to provide the electrical insulation. To ensure a good electrical contact between the electrodes and the sample a fixed load was put up over a upper electrode. The whole assembly was enclosed in a light tight box.

Table 1. Experimental details and values of E

Sample No.	Concentration of Pd Wt. %	Method of Analysis Activation energy (eV.)	
		Initial rise E_1	Cowell and Woods E_2
S_1	0 00	0·70	0·72
S_4	0·00075	0·69	0·70
S_5	0 0025	0·68	0·65
S_9	0 025	0 65	0 69
S_{12}	0 1	0 70	0·73
S_{13}	0·25	0·69	0 66
S_{11}	0 5	0 67	0 65

The phosphor was first heated so as to empty the traps and then allowed to cool in dark It was then excited by the ultraviolet radiation (3650 Å Hg doublet) for five minutes and left for decay for fifteen minutes The sample was heated at constant heating rate (0 54 °K/S.) and the resulting current was fed to a potentiometric recorder on which TSC curves were recorded The heating of the samples with a uniform rate was achieved by an electric linear temperature programmer (Telmax, Type-TEL-PRO-100).

3 Results and Discussion

Figure 1 shows a set of 7 TSC curves obtained for samples containing varying concentration of Pd All the TSC curves exhibited single peak in the temperature region studied. The curves are plotted after normalizing the maximum current to a value 100 and shifting their ordinates suitably to avoid overlapping and rendering their comparison easier

It is evident from figure 1 that the shape of TSC curves and also their peak positions are not significantly affected by the activator concentration Whatever variation observed is unsystematic and is also relatively small

From TSC curves, the activation energy E can be estimated in several ways (Nicholas & Woods 1964, Saunders 1969) In the present investigation two different methods were used. The first method followed is the initial rise method (Garlick & Gibson 1948) where thermally stimulated conductivity 6, for all types of kinetics (Nicholas & Woods 1964), is expressed in the form

$$\ln 6 = -\frac{E}{KT} + \text{constant}, \qquad \ldots (1)$$

A plot of $\ln G$ against $1/T$ is a straight line having slope equal to E/K. The values of activation energies calculated in this way are denoted by E_1 and are shown in table 1.

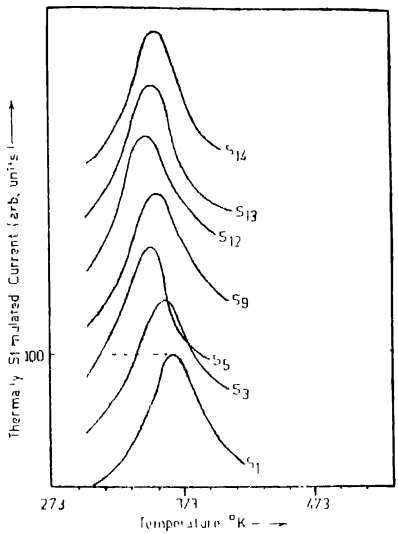

Fig. 1. TSC curves for samples containing varying concentration of Pd.

The second method used to compute the activation energies is due to Cowell & Woods (1967) and is a curve fitting technique. The method is based on the fact that for first order TSC curve G is related to E by the relation

$$G = A \exp\left[-\frac{E}{KT} - B \exp\left(-\frac{E}{KT}\right)\left(\frac{E}{KT}\right)^{-2}\right] \tag{2}$$

and for second order by

$$G = C \exp\left[-\frac{E}{KT} - D \exp\left(-\frac{E}{KT}\right)\left(\frac{E}{KT}\right)^{-7/2}\right], \tag{3}$$

where A and C are constants,

$$B = \exp\left(\frac{E}{KT_m}\right)\frac{(E/KT_m)^2}{(E/KT_m)+2}, \tag{4}$$

$$D = \frac{\exp(E/KT_m)(E/KT_m)^{9/2}}{(E/KT_m)+3.5} \tag{5}$$

and T'_m is the peak temperature The value of E evaluated by the initial rise method was used as approximate value for curve-fitting procedure and was adjusted to obtain the best fit It has been found that the best fit to the TSC curves is obtained by the use of eq. (2). The values of E thus evaluated are denoted by E_2 and are shown in table 1. From the table 1 it may be seen that the E values given by two analysis agree reasonably well.

The addition of activator (Pd) in the present system of phosphors does not change the form of the TSC curves and also does not give rise to new TSC peaks in the temperature region studied. Moreover the variation observed in the values of E (table 1) is also negligibly small and unsystematic This indicates that the addition of activator only modifies the relative importance of traps responsible for TSC, but not their mean depths (Sinha & Sivaraman 1972) The best fit obtained to the TSC curves by the use of eq. (2) suggests that probable type of kinetics involved in the recombination process of these phosphors is first order. This is supported by the photo and thermoluminescence studies reported earlier on these samples (Lawangar & Narlikar 1975).

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